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ABSTRACT

Direct multicomponent analysis of malodorous volatile organic compounds (VOCs) present in ambient air samples from 29 swine (*Sus scrofa*) production facilities was used to develop a 19-component artificial swine odor solution that simulated olfactory properties of swine effluent. Analyses employing either a human panel consisting of 14 subjects or gas chromatography were performed on the air stream from an emission chamber to assess human olfactory responses or odorant concentration, respectively. Analysis of the olfactory responses using Fisher's LSD statistics showed that the subjects were sensitive to changes in air concentration of the VOC standard across dilutions differing by approximately 16%. The effect of chemical synergisms and antagonisms on human olfactory response magnitudes was assessed by altering the individual concentration of nine compounds in artificial swine odor over a twofold concentration range while maintaining the other 18 components at a constant concentration. A synergistic olfactory response was observed when the air concentration of acetic acid was increased relative to the concentration of other VOC odorants in the standard. An antagonistic olfactory response was observed when the air concentration of 4-ethyl phenol was increased relative to the other VOC odorants in the standard. The collective odorant responses for nine major VOCs associated with swine odor were used to develop an olfactory prediction model to estimate human odor response magnitudes to swine manure odorants through measured air concentrations of indicator VOCs. The results of this study show that direct multicomponent analysis of VOCs emitted from swine effluent can be applied toward estimating perceived odor intensity.

Modern swine management practices have undergone extensive changes during the last two decades in an effort to improve animal production efficiency, reduce animal mortality, and provide safer, higher quality animal products (Barker et al., 1996). These improvements in production efficiency have transformed the infrastructure of the swine industry, and have permitted the effective management of larger populations of animals on production sites. The expansion of concentrated animal feeding operations (CAFOs) throughout the USA has catalyzed an increased awareness by the general public and governmental agencies for the potential effects of these facilities on water and air quality (Schiffman et al., 1995; Thu et al., 1997). Recent air quality studies have shown that CAFOs can adversely affect air quality through the release of odor (Jacobson et al., 1997b; Zahn et al., 2001) and odorous compounds such as hydrogen sulfide (H_2S) (Jacobson et al., 1997a), ammonia (NH_3) (Asman, 1995; Eklund and LaCosse, 1995; Sharpe and Harper, 1998), and volatile organic compounds (VOCs) (Zahn et al., 1997; Zahn et al., 2001).

Efforts to remediate odor from swine production facilities have been impeded by the lack of instruments capable of high-throughput, objective odor measurements. The desire to develop high-throughput, inexpensive methods of odor quantification has been the impetus for several recent investigations that have focused on defining relationships between gas concentration of odorants emitted from animal manure and odor intensity measured by olfactory methods (Hobbs et al., 1995; Jacobson et al., 1997a,b; Obrock-Hegel, 1997; Pain et al., 1990; Zahn et al., 2001). Obrock-Hegel (1997) found that nutritional manipulation of amino acid intake reduced NH_3, cresols, and indoles measured in air samples from production environments. However, no reduction in odor concentration was observed between control and treatment samples. Schulte et al. (1985) and Hobbs et al. (1995) linked high levels of NH_3 to odor. Unfortunately, the latter authors noted that the relationship

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Abbreviations: VOC, volatile organic compound; CAFO, concentrated animal feeding operation.

between NH_3 and odor could not be universally applied to all farms, especially when they differed in the type of manure management system used. The use of H_2S as a surrogate of livestock waste odor has also proven to be a formidable challenge. Jacobson et al. (1997b) evaluated odor and H_2S concentration in air from approximately 60 different pig, dairy, beef, and poultry manure storage units on farms in Minnesota. Low correlation was observed between H_2S and odor concentration for manure storages based on a species comparison and for production systems grouped according to manure management system type (pit, basin, and lagoon). The study further suggested the possibility that chemical odorants other than H_2S (i.e., VOCs) were responsible for swine odor. In support of these findings, Powers et al. (1999) recently demonstrated that solution-phase concentrations of several VOCs present in anaerobic digester effluent were positively correlated with odor intensity. However, the solution-phase concentration of VOCs did not predict odor intensities well enough to suggest that human panels should be eliminated. Data quality in the latter study were probably adversely influenced by the fact that odor responses were correlated to solution-phase concentrations of odorants, rather than to direct measurements of odorants present in air samples presented to panelists. Previous studies have established the importance of using air-phase concentrations of odorants when performing correlations to odor concentration, since VOC volatilization rates are highly matrix dependent (Hobbs et al., 1995; MacIntyre et al., 1995; Zahn et al., 1997). Problems associated with matrix-dependent odorant volatilization were recently overcome by performing direct multicomponent analyses of air samples that were simultaneously evaluated for odor intensity by human panels (Zahn et al., 2001). By using this sampling approach, it was shown that odor intensity from 29 swine production facilities correlated strongly ($r^2 = 0.88$) to the concentration of 19 volatile organic compounds present in ambient air samples. While this study provided evidence that direct multicomponent analysis of VOCs may be useful in monitoring odor from swine production, several important details concerning olfactory properties of key VOC odorants and the behavior of these compounds in complex mixtures were not addressed in this study.

The aims of this study are similar to that of Zahn et al. (2001) in our desire to develop an instrument-based odor quantification method for CAFOs that is based on the air concentration of specific odorants. In addition to this aim, there is currently a need to define olfactory properties of odorant reference standards that were previously described by Zahn et al. (2001). The objectives of this study were to (i) validate the selection of odorants present in synthetic swine odor by comparing the chemical profile of the synthetic mixture with the chemical profile of stored swine manure samples; (ii) construct and validate an emission chamber for reproducible delivery of an air stream containing the indicator odorants to an absorbent tube or to a nose cone for chemical and olfactory evaluation, respectively; (iii) define organoleptic properties of the odorant mixture at different delivery concentrations; and (iv) define potential synergistic and antagonistic olfactory activities for this group of odorants.

MATERIALS AND METHODS

Composition of Odorant Solutions

Sensory responses were measured for solutions containing 19 volatile organic compounds that were previously correlated to odor from commercial swine production facilities (Zahn et al., 2001). The chemical composition of synthetic swine odor Z2 was optimized in a laboratory dynamic flux chamber to mimic emission parameters for VOCs emitted from manure collected from a high-odor, Type 1 swine manure management system (Zahn et al., 2001). The synthetic swine odor solution Z2 (Zahn and DiSpirito, 1999) consisted of 0.05 m*M* dimethyl disulfide, 8 m*M* acetic acid, 3.5 m*M* propionic acid, 0.5 m*M* isobutyric acid, 0.4 m*M* 2-butanol, 1.4 m*M* butyric acid, 0.2 m*M* isovaleric acid, 0.5 m*M* valeric acid, 0.1 m*M* isocaproic acid, 0.2 m*M* caproic acid, 0.2 m*M* heptanoic acid, 0.1 m*M* indole, 0.15 m*M* 3-methyl indole, 0.2 m*M* 4-methyl phenol, 0.12 m*M* 4-ethyl phenol, 0.15 m*M* phenol, 0.1 m*M* benzyl alcohol, 0.15 m*M* 2-amino acetophenone, 0.1 m*M* butylated hydroxytoluene (added as a preservative), and 8 m*M* ammonium acetate. Pure compounds (Aldrich Chemical Co., Milwaukee, WI) were dissolved in warm (45°C) double distilled water (ddH_2O) while stirring and the solution pH was frequently adjusted to pH 7.0 with 2 *M* potassium hydroxide.

The reference stimulus solution was produced by diluting synthetic swine odor solution Z2 in an equal volume of ddH_2O. Odorant solutions were formulated within 1 h of human evaluation to reduce variation due to loss of the odorants through volatilization or chemical decomposition, and were maintained at 21.0 ± 1.1°C during all procedures. Two series of experimental stimuli were formulated for olfactory studies. First, the effect of odorant concentration on olfactory responses was evaluated by preparing by six dilutions (83, 67, 50, 33, 17, and 1%) of synthetic swine odor solution Z2 in ddH_2O. Second, the effect of synergistic or antagonistic interactions between odorants was investigated by doubling the concentration of individual odorants present in synthetic swine odor Z2, while maintaining the remaining 18 odorants at concentrations equivalent to the reference stimulus solution. The latter odorant solutions were diluted over the same concentration range (100, 83, 67, 50, 33, 17, and 1%) that was used in the first series of experiments.

The dilutions used in this study were assigned empirically based on the olfactory responses of panelists to the various dilutions of the synthetic swine odor solution. Physiological responses ranged from barely detectable to an overwhelming or unbearable olfactory response. There were five dilutions equally scattered between the two stimuli to provide data needed for fitting of olfactory response models. Statistical analysis of data shows that the dilutions employed in these experiments fitted well to established olfactory response models.

Emission Chamber Design and Operational Parameters

Olfactory and chemical quantification of VOC odorants was performed on the gas stream emitted from the dynamic emission chamber shown in Fig. 1. Compressed air from a cylinder (ultra-high purity) was passed over activated carbon (#24,226-8; Aldrich Chemical Co.) and then was introduced to the dynamic emission chamber at a height of 10 cm above

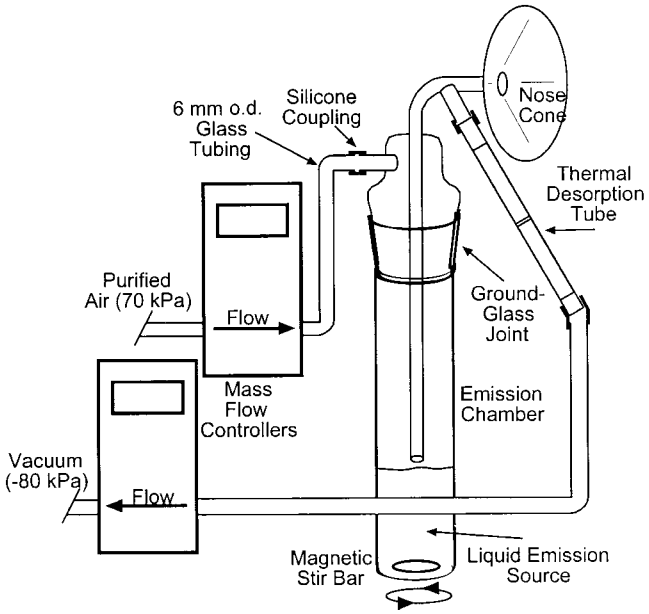

Fig. 1. Design of the dynamic emission chamber.

the odorant solution. Olfactory and chemical controls performed on chambers containing ddH_2O showed that the emission chamber, flow path, and air source had no detectable odor or VOCs in the absence of odorant solutions. The flow of clean air was maintained at 1000 mL min^{-1} (±1.2%) using a thermal mass flow controller (Series 810, Sierra Instruments, Monterey, CA). The flow of air through the chamber proceeded downward toward the surface of the odorant solution and then exited the emission chamber through a glass transfer tube that was positioned 1 cm from the surface of the odorant solution. The odorant-containg gas was forced up the transfer tube to a nose cone and sampling tee for olfactory and chemical analyses, respectively. The sampling tee was positioned at the base of the nose cone to eliminate potential discrepancies between olfactory and chemical measurements due to nonequivalent flow paths.

Odorant solutions (50 mL) and a single 1.5-cm magnetic stir bar were introduced into the chamber through a ground-glass joint at the top of the chamber. The chamber was then closed and fixed on a magnetic stir plate inside a cabinet (3.0 m^3) equipped with an exhaust fan (exhaust rate = 3.1 m^3 min^{-1}). The diameter of the emission chamber was 3.50 cm and the active surface area for the odorant solution was 9.62 cm^2. Upon startup of the dynamic emission chamber, the initial 5 min (~5 L of odorant-containing gas) of operation were dedicated to equilibrating the flow path to odorants present in the gas stream. During this equilibration period the exhaust fan was operated to remove odorants from the cabinet. After the equilibration period, the fan was shut off and the air stream was sampled by human panelists or by chemical methods. Chemical and human olfactory analyses were conducted separately in order to minimize potential interferences with human olfactory evaluations. Olfactory evaluations of odorant air streams were conducted using full air flow through the dynamic emission chamber (1000 mL min^{-1}). The exhaust fan was operated for 1 min after each evaluation to remove residual odorants from the sampling area. Air temperature and relative humidity in the evaluation area were maintained at 21.0 ± 1.1°C and 62 ± 7% RH, respectively. Comparisons between the reference stimulus and experimental stimuli were performed by placing a second dynamic emission chamber in the evaluation cabinet at a distance of 0.35 m from the reference stimulus. The second chamber is referred to as the *experimental stimulus*.

Volatile organic compounds in the air stream from the emission chamber were trapped on adsorbent resins at the sampling tee using a flow rate of 950 mL min^{-1}. The remaining balance of the gas flow (50 mL min^{-1}) was expelled through the unoccupied nose cone. The adsorbent resins consisted of a multibed combination of Tenax TA and Carboxen-569 (Supelco, Bellefonte, PA) as previously described by Zahn et al. (1997). Compounds captured on the adsorbent tubes were transferred to a gas chromatograph by thermal desorption, separated on a Hewlett–Packard (Palo Alto, CA) Innowax cross-lined polyethylene glycol capillary column (30 m × 0.25 mm), and detected by flame ionization or by a mass selective detector as previously described by Zahn et al. (1997).

Scale Development and Sensory Panel Design

Development of a scale to measure the effects of odorant concentration was completed using Steven's magnitude estimation technique with 14 human panelists (Stevens, 1957, 1961, 1962). Subjects were presented with an odorant air stream from an emission chamber containing the reference stimulus solution and were instructed that the stimulus had an intensity value of 100 (arbitrary) odor intensity units. Panelists were then instructed to sample an air stream from a second chamber (experimental sample) and to score the intensity of the odor relative to the reference stimulus. For example, if the subject perceived that the intensity of an experimental sample was half that of the reference stimulus, then a value of 50 was reported for the experimental sample. If the subject perceived that the odor was 75% more intense than the reference stimulus then a value of 175 was reported for the experimental sample. Odor intensity scores were reported between a range of 0 and 200 relative odor intensity units.

Magnitude estimation studies have shown that the perceived magnitude of a stimulus is a power function of the intensity of the stimulus (Stevens, 1957, 1961, 1962). The mathematical relationship between perceived magnitude and physical intensity of the stimulus (Steven's Law) is:

$$P = k \times I^b$$

where P = the experimentally defined perceived magnitude of a stimulus, k = a stimulus-dependent constant that represents the intercept of the line function, b = a stimulus-dependent constant that represents the slope of the line function, and I = the actual physical intensity of the stimulus (odorant concentration).

The magnitude estimation technique was used with a human panel of 14 subjects. The panel ranged in age from 18 to 40 yr and was composed of an equal number of male and female subjects to minimize gender bias. In the first stage of the study, subjects were presented with synthetic swine odor solution Z2 and five dilutions of the solution (100, 83, 67, 50, 33, 17, and 1%) as described in the Composition of Odorant Solutions section. The solutions were placed in emission chambers with encrypted labels and then were fixed in the experimental stimulus position for evaluation. Individuals on the panel were instructed to score the physical intensity of each experimental stimulus relative to the reference stimulus. In subsequent stages of the study, the panel was presented with nine different experimental stimuli, differing only in the concentration of a single odorant. The concentration of a single odorant in the solution was doubled from the original concentration value, while other odorants (the remaining 18) present in the solution were unchanged. Solutions were again diluted over a concentration range from 100 to 1%, and then placed in emission

chambers for presentation to the panel. The following nine VOCs were evaluated for potential synergistic–antagonistic activity: acetic acid, isobutyric acid, butyric acid, valeric acid, heptanoic acid, phenol, 4-methyl phenol, 4-ethyl phenol, and 3-methyl indole. These nine VOCs were selected based on their universal presence in air samples from swine production facilities and/or due to their low olfactory detection thresholds.

The order in which the first 12 subjects sampled the odorants was balanced using a Latin Square to reduce sampling bias. Panelists evaluated each experimental stimulus twice during individual sessions. Each subject would compare the experimental stimulus with the reference stimulus in one serial order, and then would be presented the same samples for a second trial in a different serial order. Thus, the effects of the presentation order could be randomized in order to reduce sampling bias. Panelists were allowed to evaluate odor stimuli as many times as they wished before reporting the stimulus score to the panel operator. Individual sampling sessions for the duplicate analysis of six experimental stimuli were completed in 15 min for individual panel members and were performed on two separate days during the same week.

RESULTS AND DISCUSSION

Development and Validation of Synthetic Swine Odor Z2

Synthetic swine odor Z2 consists of a buffered mixture of volatile organic compounds in an aqueous solution. The constituents of this solution were selected based on the qualitative analysis of ambient air samples (n = 328) collected from 29 swine production facilities located in Iowa, North Carolina, and Oklahoma (Zahn et al., 1997, 2001). Ambient air samples for these studies were collected on the downwind edge or center of outdoor manure collection systems (lagoons and basins) at approximately 1.5 m from the emitting surface. The concentration of compounds in the solution was determined empirically by comparing emission profiles from liquid samples of swine manure collected from the 29 sites with the emission profiles from mixtures of pure odorants using the dynamic emission chamber. A series of chromatograms collected for one comparison is shown in Fig. 2. The identity and properties of compounds separated in these chromatograms are described in Table 1.

A comparison between the mean air concentration of odorant compounds collected from the atmosphere above swine manure management systems with published odor threshold values is shown in Table 1. The fact that the mean air concentration for hydrogen sulfide and 2-butanol were below the odor threshold value indicates that these compounds do not contribute significantly to odor associated with swine manure. This finding corroborates earlier field studies by Jacobson et al. (1997a,b), which showed a poor correlation between odor concentration and the concentration of hydrogen sulfide in emission plumes from swine production facilities. The mean air concentration of other VOC odorants present in emission plumes from swine production facilities was found to range between a level equal to the odor threshold value to almost 4000-fold above the odor threshold value (Table 1). These findings provided evidence that VOCs may be responsible for a significant proportion of the odor present in emission plumes from swine production facilities. In addition to the use of chemical methods for the purpose of validating the composition of synthetic swine odor, qualitative odor characteristics of the solution were determined for odor

Table 1. Odor characteristics, olfactory thresholds, and recommended exposure limits for volatile organic compounds identified from air samples at swine production facilities.

Chromatographic peak #, organic compound	Average air conc.†	Ref.‡	Odor characteristic	Odor threshold§	Recommended TWA limits¶
	mg m^{-3}			mg m^{-3}	
Hydrogen sulfide	0.090	1	rotten eggs	0.140	14
Ammonia	3.70	1	sharp, pungent	0.027–2.2	18
1. Dimethyl disulfide	0.017	1	putrid, decayed vegetables	0.0011–0.61	–
2. 2-Butanol	0.019	1	alcohol	0.11	305
3. Dimethyl trisulfide	0.013	1	nauseating	0.0072–0.023	–
4. Acetic acid	0.270	2	pungent	0.1–2.5	25
5. Propionic acid	0.130	2	fecal	0.0025	30
6. Isobutyric acid	0.110	2	fecal	0.00072	–
7. Butyric acid	0.590	2	fecal, stench	0.00025	–
8. Isovaleric acid	0.098	1	fecal	0.00017	–
9. *n*-Valeric acid	0.360	1	fecal	0.00026	–
10. Isocaproic acid	0.010	1	stench	0.0020	–
11. *n*-Caproic acid	0.110	2	fecal	0.0020	–
12. Heptanoic acid	0.008	1	pungent	0.0028	–
13. Butylated hydroxytoluene	–	–	nd	nd	–
14. Benzyl alcohol	0.002	2	alcohol	nd	–
15. Phenol	0.025	2	aromatic	0.23–0.38	19
16. 4-Methyl phenol	0.090	2	fecal	0.0021–0.009	22
17. 4-Ethyl phenol	0.004	2	pungent	0.0035–0.010	25
18. 2-Amino acetophenone	0.001	2	fruity, ammonia	nd	–
19. Indole	0.002	1	fecal	0.0019	
20. 3-Methyl indole	0.002	1	fecal, nauseating	0.0000005–0.0064	–

† Average reported concentration of the analyte in air at a height of 1.5 m from the surface of a high-odor swine manure basin. Butylated hydroxytoluene added as a preservative.
‡ References: 1 = Zahn et al., 2000; 2= Zahn et al., 1997.
§ Milligrams of analyte per cubic meter of air at standard temperature and pressure. nd = not determined.
¶ The time-weighted average concentration for a normal 8-h workday and a 40-h workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect (Plog, 1988 p. 770–783).

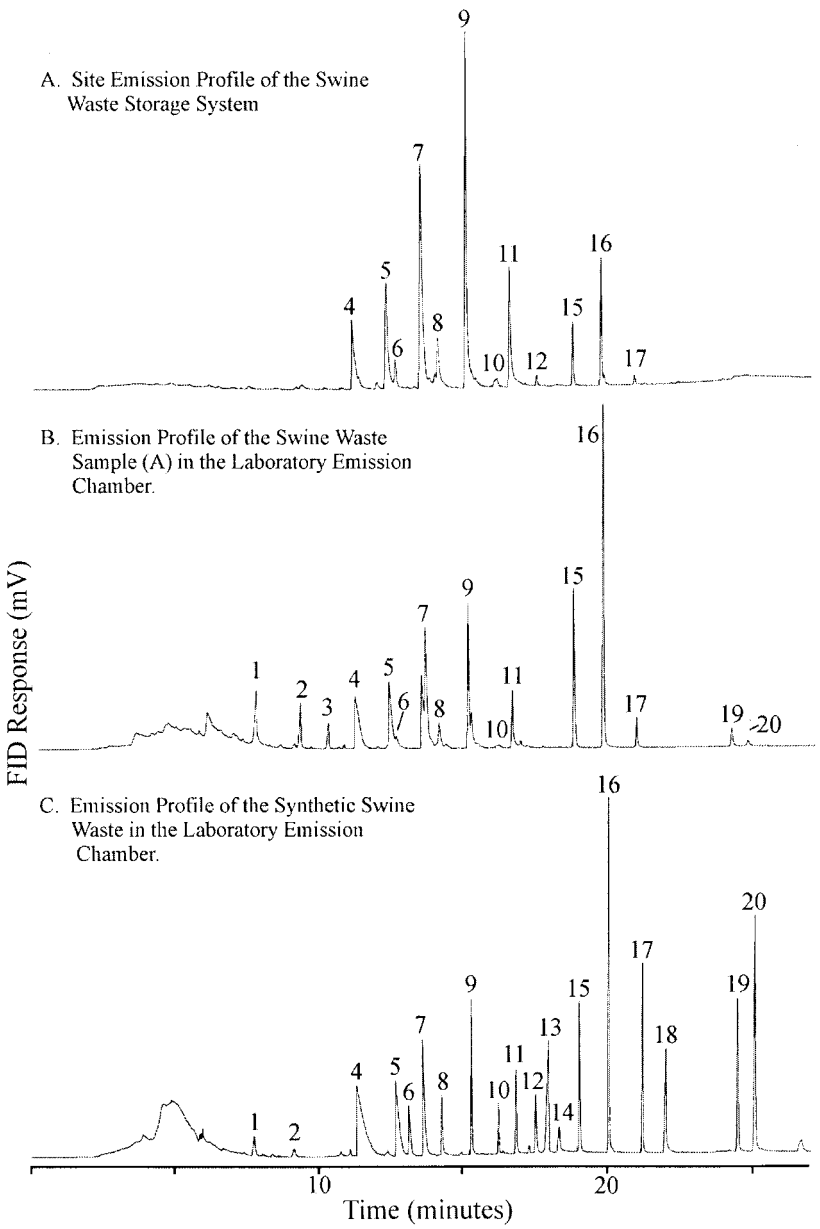

Fig. 2. Chromatographic profiles of organic compounds present in (*A*) an air sample taken in the odor plume from a high-odor swine manure basin, (*B*) a liquid sample taken from the same basin in *A* and then placed in the dynamic emission chamber, and (*C*) synthetic swine odor Z2 placed in the dynamic emission chamber. Chamber operation parameters were identical for samples *B* and *C*. Chromatographic peak reference numbers correspond to compounds listed in Table 1.

solution Z2 and for six dilutions of this solution by a human panel. Results from these qualitative evaluations indicated that few of the compounds had a distinct manure odor character when evaluated on an individual basis; however, the collective odorant properties of VOCs present in the synthetic swine odor solutions were found to simulate olfactory properties of swine manure odor (Table 2).

More than 200 volatile organic compounds have been identified from liquid swine manure and from anaerobic headspace analysis of swine manure. Field studies, however, have shown that only a fraction of these compounds can routinely be detected in emission plumes from these point sources (Zahn et al., 1997, 2001). Efforts to characterize VOCs in emission plumes from animal production environments have been impeded by the chemical diversity of odorants, the reactivity of odorants, and by the extremely low concentration of these odorants in emission plumes (Zahn et al., 1997). Air monitoring methods established by the USEPA for assessing VOC emissions from industrial–commercial point sources (i.e., TO14) were found to require modification in order to provide the level of sensitivity necessary for detection and quantification of key odorant compounds (Zahn et al., 1997, 2001). These method modifications often involved optimizing or refitting sample concentration or water–carbon dioxide management systems in order to allow for the efficient desorp-

Table 2. Character descriptors associated with synthetic swine odor solutions. Odorant concentrations are reported as a percent of synthetic swine odor Z2.

1%	16%	32%	50%	67%	83%	100%
Barely detectable	Stinky	Mildly smelly	Unpleasant	Smelly	Strong	Very bad
Nothing	Sweeter	Moderate	Wet socks	Pungent	Very unpleasant	Strong
Noticeable	Not all that unpleasant	Gross	Foot odor	Sweet	Annoying	Powerful
Barely present		Feces-like	Slightly bothersome	Bothersome	Acidic	Headache
Moderate	Mild		Rotting garbage	Powerful	Bothersome	Very unpleasant
Sweet smelling	Somewhat bothersome			Really bad	Garbage	Ammonia
Very mild						Potent
Slightly unpleasant	Dense					Sickening
Mildly unpleasant	Obvious odor					Very acidic
	Pungent					Dizzying
						Very bothersome
						Astringent

tion of high boiling point or water soluble compounds. Commercially available analytical systems for VOC concentration and for water–carbon dioxide management were found to be well suited for the analysis of non-water soluble analytes with low boiling points and relatively high Henry's law constants (i.e., halogen hydrocarbons, alkanes, alkenes, and aromatic solvents), but often did not provide quantitative results for analysis of the 19 VOCs associated with swine odor.

In addition to the 19 compounds in synthetic swine odor Z2, a number of other odiferous compounds, such as amine and sulfide-containing compounds, have been correlated with swine manure odor based on solution-phase measurements (Yasuhara et al., 1984). However, with the exception of hydrogen sulfide, organic sulfide and organic amine-containing compounds were not routinely detected in emission plumes from swine production facilities (Zahn et al., 1997, 2001). It has been well established that sulfides and amines are inherently unstable in oxidized atmospheres due to their high chemical reactivity. Sulfides are weak monoprotic and polyprotic (H_2S) acids that are highly reactive under aerobic conditions and neutral pH. Ammonia and amines, on the other hand, are weak bases that play a major role in neutralization of sulfur dioxide and nitrogen oxides in the atmosphere (Harper and Sharpe, 1997). Acid–base neutralization of air pollutants has been shown to produce salts that contribute to chemically generated particulate matter in the atmosphere. While there is currently little direct evidence to explain the absence of these compounds in emission plumes, the presence of high concentrations of disulfides such as dimethyl disulfide (the oxidation product of methyl mercaptan) and dimethyl trisulfide (the oxidation product of hydrogen sulfide and methyl mercaptan) provides indirect evidence that free sulfides are readily oxidized in the atmosphere or during sample collection and analysis procedures. In contrast to the labile nature of sulfide and amine-containing compounds, VOCs in synthetic swine odor Z2 exhibit a higher level of chemical stability. Additionally, these compounds were observed to exhibit high atmospheric transport coefficients that permitted long-range atmospheric transport under unstable atmospheric conditions (Zahn et al., 1997). These findings indicate that the compounds present in the synthetic swine odor Z2 represent ideal odorants for use in swine odor research.

Operational Parameters of the Dynamic Emission Chamber

The ability to maintain a constant emission rate of VOCs at the olfactory sampling port during the course of the olfactory evaluation period was considered a critical element in the success of the study. Therefore, preliminary investigations were conducted on synthetic swine odor solutions that were placed in the dynamic emission chamber to determine: (i) if the emission rate of VOCs release from the dynamic emission chamber was constant over a typical olfactory sampling period and (ii) if emission rate of VOCs was proportional to the concentration of VOCs present in the liquid phase of the emission source. The emission rate of 19 VOCs present in synthetic swine odor Z2 was measured by trapping the airborne analytes on adsorption tubes over time intervals and by determining the change in concentration of VOCs present in the liquid over the same time period. Adsorption samples were collected over a 3-h period in 0.5-h intervals from air emitted from the dynamic emission chamber. The cumulative emission rates of acetic acid, 4-methyl phenol, and 4-ethyl phenol over the 3-h sampling period are shown in Fig. 3. The linear shape of the fitted line ($r^2 > 0.97$) shows that the emission rate for each VOC remained nearly constant during the sampling period. Analysis of the concentration of the other 16 compounds in air samples showed that the emission rate of these compounds also remained nearly constant over the 3-h collection period. The concentration of VOCs present in liquid phase of synthetic swine odor solution Z2 was reduced between 0.05 to 4.0% over the 3-h collection period. Compounds such as dimethyl disulfide that had a relatively low source concentration and a high Henry's law constant showed the greatest change in solution concentration over the sampling period (4.0%), while compounds with lower volatility (benzyl alcohol, 0.1%) or high source concentration (acetic acid, 0.05%), exhibited less change in solution concentration over the sampling period. Comparison of the total amount of VOCs recovered by adsorption tubes with the losses of analytes measured in the solution phase showed that between 94 and 99% of the VOCs emitted from the solution could be recovered and quantified by the thermal desorption–gas chromatography method. The mean emission rate values for four independent emission rate experiments conducted using the 19 odorant compounds are shown in Table 3.

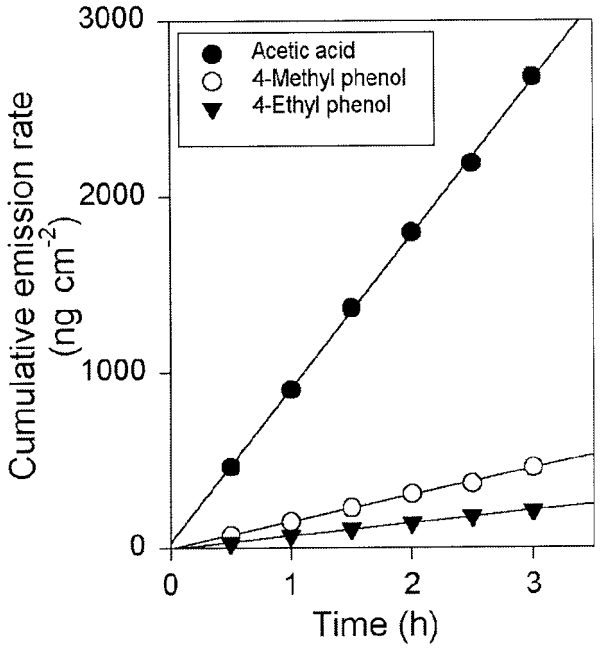

Fig. 3. The emission rate of select VOCs in synthetic swine odor Z2 from the dynamic emission chamber over a 3-h operation period.

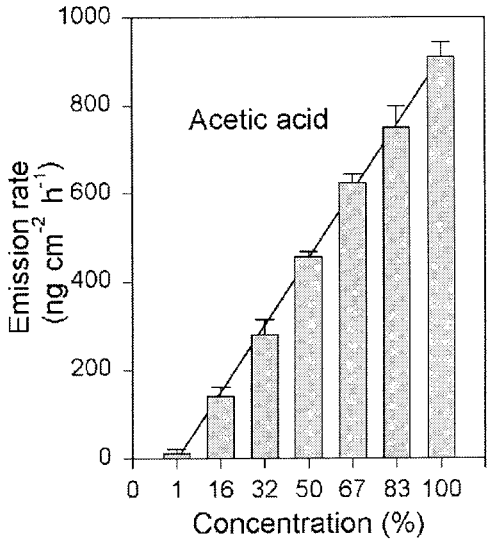

Fig. 4. The effect of solution concentration on emission rate of acetic acid from the emission chamber over a 1-h sampling period. The mean and standard deviation for four independent samples at each concentration of the odorant solution is shown.

The effect of the solution concentration on VOC emission rate was tested for each of the seven VOC concentrations used in olfactometric trials. Solution concentration of acetic acid was found to be proportional to the emission rate of acetic acid over the concentration range tested (Fig. 4). The relationship between solution concentration and emission rate of all other VOCs present in synthetic swine odor solutions was observed to be essentially identical to the emission behavior exhibited by acetic acid. These results indicate that the emission chamber delivers a highly reproducible and relatively constant concentration of odorants to the nose cone during the length of time that was required to complete olfactory evaluations of the odorant samples.

Panel and Scale Development

Three olfactometric trials (n = 504) were conducted on the synthetic swine odor Z2 and the six serial dilutions of this stimulus using a human panel of 14 individuals. The mean perceived magnitude of stimuli (P) and the physical intensity of stimuli (I) for individual trials were analyzed to determine fit to Stevens' Law (see Materials and Methods section for equation). The best-

Table 3. Emission rate of volatile organic compounds (VOCs) from artificial swine odor Z2 under the operation conditions described in the Materials and Methods section. Reported values represent the mean from four independent samples with the standard deviation <4% of the mean.

Chromatographic peak #, organic compound	Solution-phase concentration of VOC	Measured VOC flux rate†	Measured VOC concentration at nose cone
	mM	ng cm^{-2} h^{-1}	μg m^{-3}
1. Dimethyl disulfide	0.05	326	52.3
2. 2-Butanol	0.4	185	29.7
4. Acetic acid	16‡	912	146.0
5. Propionic acid	3.5	285	45.7
6. Isobutyric acid	0.5	88	14.2
7. Butyric acid	1.4	212	34
8. Isovaleric acid	0.2	59	9.5
9. *n*-Valeric acid	0.5	141	22.7
10. Isocaproic acid	0.1	43	6.8
11. *n*-Caproic acid	0.2	81	13.0
12. Heptanoic acid	0.2	67	10.7
13. Butylated hydroxytoluene	0.1	67	10.7
14. Benzyl alcohol	0.1	26	4.2
15. Phenol	0.15	130	21.0
16. 4-Methyl phenol	0.2	153	24.5
17. 4-Ethyl phenol	0.12	70	11.2
18. 2-Amino acetophenone	0.15	98	15.7
19. Indole	0.1	63	10.2
20. 3-Methyl indole	0.15	112	18.0

† Operational parameters for the dynamic emission chamber during the emission measurements were: flow rate = 950 mL min^{-1} (total chamber flow = 1000 mL min^{-1}), sampling period = 60 min, air and solution temperature = 21°C, relative humidity = 62%, and active surface area of emission chamber = 9.62 cm^2.

‡ Combined concentration from acetic acid and ammonium acetete.

Table 4. Fitting equation for the perceived odor intensity of synthetic swine odor solutions (standard) and for odorant solutions containing a twofold concentration of individual odorants.

Odorant	Equation	Measured variance (r^2)
Standard	$P = 36.60\ I^{0.265}$	0.921
Standard + valeric acid	$P = 21.92\ I^{0.413}$	0.994
Standard + butyric acid	$P = 19.09\ I^{0.432}$	0.959
Standard + heptanoic acid	$P = 38.20\ I^{0.283}$	0.974
Standard + acetic acid	$P = 40.79\ I^{0.300}$	0.983
Standard + isobutyric acid	$P = 27.21\ I^{0.344}$	0.985
Standard + 4-methyl phenol	$P = 32.34\ I^{0.307}$	0.997
Standard + 4-ethyl phenol	$P = 27.42\ I^{0.310}$	0.985
Standard + 3-methyl indole	$P = 25.32\ I^{0.371}$	0.952
Standard + phenol	$P = 32.33\ I^{0.304}$	0.943

fit equation for these samples and for samples containing a twofold higher concentration of individual analytes is shown in Table 4. Analysis of variance for each of the odorant series shows that the data conformed well to Stevens' Law and that variance in these measurements was minimal.

Several points should be noted in the analysis of Table 4. First, the value of b (the power to which I is raised) provides a measure of the slope of the best fitting curve. Higher values of b indicate greater slope meaning that mixtures with a high b value (i.e., standard + butyric acid, $b = 0.432$) were more affected by concentration changes than mixtures with a low b value, such as standard + heptanoic acid ($b = 0.283$). Also of interest is the fact that the values of b range from 0.265 to 0.432 with a mean of 0.333. Different senses can vary widely in their b values. For example, for judging the brightness of a light, the b value is approximately 0.3, while for judging the strength of electric shock, the b value is approximately 3.5 (Schiffman, 1982). Previous olfactory research conducted on evaluating the odor intensity of coffee and heptane has reported b values near 0.5 (Stevens, 1961, 1970, 1975). The results of this study show that synthetic swine odor has values of b that are comparable with the studies of other odorants (Cain et al., 1998; Degel and Koster, 1998; Liden et al., 1998; Livermore and Laing, 1998).

Also of interest were the extremely high values of r^2 that were obtained for analysis of variance. Analysis of variance showed that Stevens' Law could explain, on average, 97% of the variation in the subjects' estimates of odor intensity. This result provides evidence that the VOC delivery system produces highly reproducible olfactory stimuli. A Within Subjects Factorial Analysis of Variance (ANOVA) was used to determine the effects of odorant concentration on the mean perceived odor intensity scores. Two factors were included in the ANOVA: (i) the effect of odorant concentration on olfactory responses over seven odorant concentrations (100, 83, 67, 50, 33, 17, and 1%), and (ii) the effect of synergistic or antagonistic interactions between nine odorants present in synthetic swine odor Z2. This analysis yielded a reliable main effect due to concentration of odorants [$F(5, 65) = 142.35$, $p < 0.0001$], a reliable main effect due to synergistic–antagonistic interactions between odorants [$F(9, 117) = 3.58$, $p < 0.001$], and a reliable interaction between concentration and synergistic–antagonistic interactions between odorants [$F(45, 585) = 3.128$, $p < 0.0001$]. Subsequent analysis of the main effects showed that several of the chemical mixtures produced reliably greater mean odor intensity ratings than others. The mean rating for each of the solutions and standard error are shown in Table 5.

Analysis of data for determining synergistic–antagonistic interactions between nine odorants present in synthetic swine odor Z2 was completed using Fisher's LSD statistic. The value of Fisher's LSD for odorant interactions was 13.52 odor intensity units, meaning that any of the mean ratings differing by more than 13.52 are reliably different. Odorant solutions containing a twofold higher concentration of acetic acid gave mean perceived odor intensity scores that were statistically higher than the standard, while solutions containing twofold higher concentrations of 4-ethyl phenol gave statistically lower odor intensity scores than the standard (Table 5). Other treatments in this series were found to be statistically equivalent.

The concentrations of odorant solutions evaluated in this study were found to elicit a strong effect on mean perceived odor intensity scores. The value of Fisher's LSD statistic for concentration data was 9.59 odor intensity units (Table 6). As such, the 1% concentration produced statistically lower mean perceived odor intensity

Table 5. Mean perceived odor intensity scores for synthetic swine odor solutions and the effect of individual odorants on the intensity score.

Odorant	Mean rating	Standard error
Standard	94.60	4.92
Standard + valeric acid	97.61	5.91
Standard + butyric acid	94.71	5.66
Standard + heptanoic acid	104.68	5.43
Standard + acetic acid	119.51	6.07
Standard + isobutyric acid	94.39	5.63
Standard + 4-methyl phenol	97.40	4.91
Standard + 4-ethyl phenol	83.26	4.94
Standard + 3-methyl indole	99.34	6.50
Standard + phenol	95.94	5.12

Table 6. Mean perceived odor intensity scores for synthetic swine odor solutions differing in stimulus concentration.

Stimulus concentration	Mean score	Standard error
%		
1	30.64	2.08
17	73.14	2.98
34	96.64	2.79
67	114.91	2.85
83	130.99	3.11
100	142.55	3.60

scores than the other five concentrations evaluated. The 17% concentration produced odor intensity scores that were statistically lower than the 34, 67, 83, and 100% concentrations. This pattern of statistical significance was observed for all subsequent odorant concentrations. Thus, the human panel was clearly sensitive to changes in concentration across all odorant concentrations used in the study.

Multiple regression analysis was performed on odorant concentration data sets and on data sets used for determining synergistic–antagonistic interactions in an attempt to predict the panel-perceived odor intensity scores based on the concentration stimulus. The mean perceived odor intensity scores reported by panelists were used as the dependent (predicted) variable for these analyses. There was a strong correlation (r^2 = 87.6) observed between predicted and authentic values for mean perceived odor intensity scores. The quality of the model for odorant concentration data sets was further corroborated by the high level of statistical significance for the analysis [$F(9, 51) = 40.14$, $p < 0.0001$]. Table 7 shows the regression coefficients for each of the nine major swine effluent odorants included in the model. Analysis of this table shows that there is a high level of significance for three odorants ($p < 0.05$) and a lower level of significance for all other terms in the model. The three odorants achieving a high level of significance were acetic acid ($p < 0.001$), 4-ethyl phenol ($p = 0.02$), and 3-methyl indole ($p = 0.04$). This result indicated that the olfactory scaling model could be further simplified by systematically omitting less significant terms from the model. However, cross validation (tests of the model on independent data sets) of simplified versions of the model, created through omission of less significant terms, resulted in models with lower regression coefficients. These results indicated that all of the terms presented in Table 7 contributed to the overall accuracy of the model. The following mathematical representation of parameter estimates from the model includes factors from VOC concentration measurements of odorant solutions evaluated by panelists. These conversion factors are required to convert model input values from units of percent stimulus to μg VOC m^{-3} of air. A human olfactory response can be predicted for air samples through the concentration of the nine VOCs. The model for swine odor intensity is:

Table 7. Mathematical model representing the relationship between the stimulus concentration for nine major odorants in synthetic swine odor Z2 and the mean perceived odor intensity.

Odorant	Coefficient	*t*	*p*
Intercept	49.97		
Valeric acid	20.16	1.59	0.12
Butyric acid	5.51	1.22	0.23
Heptanoic acid	47.33	1.49	0.14
Phenol	7.82	0.19	0.85
4-Methyl phenol	22.75	0.67	0.51
Acetic acid	3.49	4.39	<0.001
Isobutyric acid	3.93	0.31	0.76
4-Ethyl phenol	−116.45	2.32	0.02
3-Methyl indole	89.57	2.16	0.04

$$\begin{aligned}\text{Odor Intensity} = {} & 50.0 + [20.2(a/22.7)] \\ & + [5.5(b/34)] + [47.3(c/10.7)] \\ & + [7.8(d/21.0)] + [22.8(e/24.5)] \\ & + [3.5(f/146.0)] + [3.9(g/14.2)] \\ & + [-116.5(h/11.2)] + [89.57(i/18.0)]\end{aligned}$$

where a = valeric acid (μg m^{-3} in air), b = butyric acid (μg m^{-3} in air), c = heptanoic acid (μg m^{-3} in air), d = phenol (μg m^{-3} in air), e = 4-methyl phenol (μg m^{-3} in air), f = acetic acid (μg m^{-3} in air), g = isobutyric acid (μg m^{-3} in air), h = 4-ethyl phenol (μg m^{-3} in air), and i = 3-methyl indole (μg m^{-3} in air). The present model provides a predicted value for odor intensity using nine of the most common volatile organic compounds found in odorous plumes from swine production. These compounds were selected from the group of 19 volatile organic compounds based on their universal presence in air samples from the several types of manure management systems used in the swine industry, their olfactory properties, and the fact that this group of odorants provided significantly higher regression coefficients for swine odor intensity models. Cross validation of the model using VOC concentration and odor intensity data from field studies of 29 swine production facilities in Iowa, Oklahoma, and North Carolina (Zahn et al., 2001) showed that the model achieved a high level of accuracy in predicting odor intensity associated with swine production facilities. Predicted values for odor intensity showed a strong correlation to actual measured values for odor intensity ($r^2 = 0.80$), and a high level of statistical significance was achieved for this validation [$(F) = 84.31$, $p < 0.0001$]. Future model improvement and validation efforts will focus on expanding the number of target analytes used in the model and on further validation of the model by performing additional VOC and odor intensity measurements at swine production sites.

Panelist training and screening is often employed in olfactory analyses to artificially restrict the range or skew the distribution of olfactory responses. Panelist training and screening is often completed using standard odorants, such as *n*-butanol, that exhibit little or no olfactory similarities to environmental odors that have been sampled. This study, for the first time, describes the composition and use of an odorant standard that more realistically simulates olfactory characteristics associated with swine production. The artificial swine odor mixture was used a standard of defined magnitude to assess the odor intensity associated with laboratory-generated swine odor samples. Using this approach, we have demonstrated that panelist training and screening was not necessary to achieve accurate quantification of the perceived odor intensity.

A field study by Zahn et al. (2001) reported that odorant concentration of 19 VOCs that were present in odor plumes from swine production facilities could be used to predict odor intensity associated with swine production. Qualitative analyses of VOCs present in air samples from four types of swine manure management systems showed that high odor intensity was associated

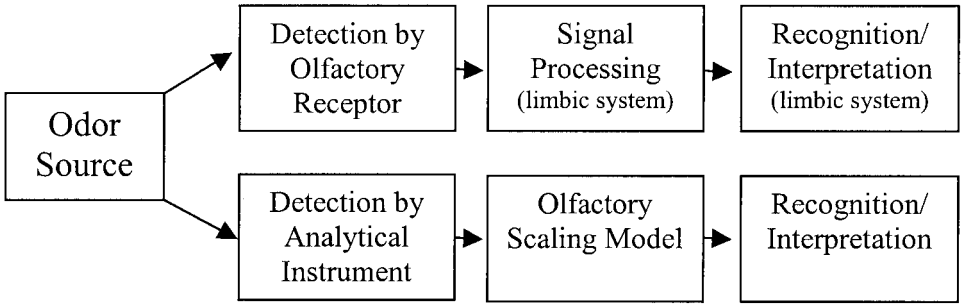

Fig. 5. A comparison of processing pathways used in odor quantification by chemical and olfactory methods.

with relatively intense gas chromatographic profiles; however, these profiles were chemically simplistic in nature when compared with the chromatographic profiles from low-odor lagoon systems that had lower concentration and higher chemical diversity. From these results, it was concluded that chemical concentration, rather than chemical diversity, was the most important factor for predicting odor intensity magnitudes associated with swine production. The results of this study provide additional support for the importance of odorant concentration as a factor in olfactory models. This study has further simplified the list of target VOC odorants from 19 in the earlier study (Zahn et al., 2001) to nine VOC odorants and has shown that synergisms and antagonisms between major odorant compounds do not appear to play a major role in measured odor intensity. This observation is important since the ability to define odorant synergisms and antagonisms has been suggested to be the most significant obstacle in applying chemical methods in odor measurement (Mackie et al., 1998). Data presented in this study provide evidence that the concentration of "specific" nonmethane VOCs that are present in air samples from swine production facilities can be applied to predict the odor intensity associated with swine production systems.

CONCLUSIONS

Anaerobic processing of livestock wastes results in the production of malodorous gases including volatile organic compounds (VOCs), hydrogen sulfide, and ammonia. Quantification of odor and trace gases from animal production facilities has traditionally been addressed in separate, unrelated research efforts due to analytical difficulties associated with the measurement of low concentrations of analytes in air samples. As a result, there is currently a lack of information concerning the ambient air concentration range and chemical identity of odorant compounds released from stored animal manure. This lack of information has impeded research efforts focused on the development of emission abatement strategies and has compelled the use of subjective, low-throughput odor measurement methods. The results of this study show that direct multicomponent analysis of VOCs present in ambient air near animal production facilities may be applied toward estimating perceived odor intensity. This instrument-based odor quantification approach would consist of (i) collecting ambient air samples from an animal production facility, (ii) determining the concentration of specific odorants present in the air sample by gas chromatography, and (iii) processing the concentration data by an olfactory scaling model in order to estimate the perceived odor intensity (Fig. 5). This instrument-based odor quantification system has been successfully applied to the quantification of odor emitted from 29 swine manure management systems in Iowa, Oklahoma, and North Carolina (Zahn et al., 2001). Results from these studies indicate that direct chemical analysis of VOCs present in air samples from animal production environments represents an alternative approach to olfactory measurements for evaluation of best management practices for swine manure management systems or as a screening method to identify swine production sites that represent a potential nuisance concern.

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